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Publication number:

**0 537 580 A2**

(12)

## EUROPEAN PATENT APPLICATION

(21) Application number: 92116943.9

(51) Int. Cl.<sup>5</sup>: C07D 401/04, C07D 401/14,  
A01N 43/56

(22) Date of filing: 05.10.92

(30) Priority: 18.10.91 JP 297772/91

(43) Date of publication of application:  
21.04.93 Bulletin 93/16

(84) Designated Contracting States:  
BE CH DE ES FR GB IT LI NL

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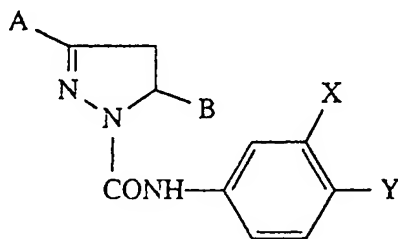
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(54) Pyrazolines as Insecticides.

(57) Novel pyrazolines of the formula (I)



wherein A represents a phenyl group which may be substituted by at least one substituent selected from the class consisting of halogen, C<sub>1</sub>-4alkyl, C<sub>1</sub>-4alkoxy and halogeno-C<sub>1</sub>-4alkyl, or A represents halogen-substituted 3-pyridyl,

B represents phenyl which may be substituted by halogen, or B represents halogen substituted 3-pyridyl,

X represents hydrogen, halogen or halogeno C<sub>1</sub>-4alkyl, and

Y represents hydrogen, halogen, C<sub>1</sub>-4alkyl or halogeno-C<sub>1</sub>-4alkyl, with the proviso that X and Y do not simultaneously represent hydrogen atom, and that at least one of A and B represents halogen-substituted 3-pyridyl.

The new compounds exhibit powerful insecticidal properties.

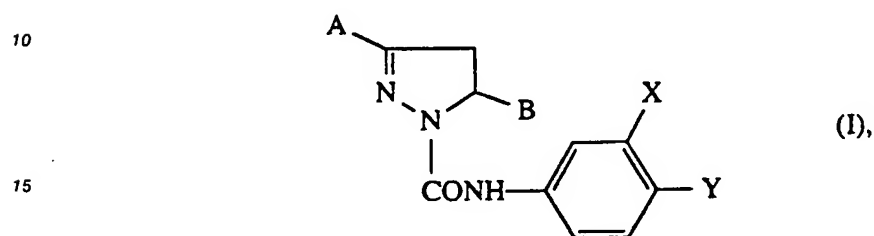
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The present invention relates to novel pyrazolines, to a process for the preparation, to their use as insecticides, as well as novel intermediates for their preparation and to a process for the preparation of those intermediates.

It has already been disclosed that a certain group of pyrazolines is useful as insecticides (see, Japanese Laid-Open patent application No. 87028/1973, which is an equivalent of DE-A 2,304,586 and of US Patent Nos. 3,991,073; 4,010,271; 4,095,026).

There have been found novel pyrazolines of the formula (I)

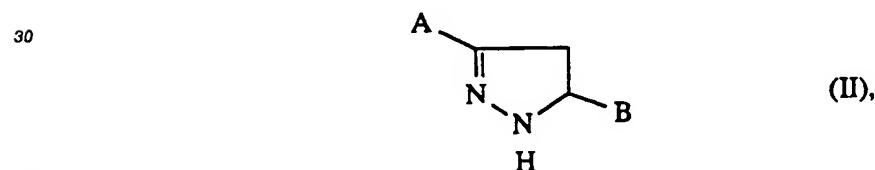


wherein A represents a phenyl which may be substituted by at least one substituent selected from the class consisting of halogen, C<sub>1</sub>-4-alkyl, C<sub>1</sub>-4-alkoxy and halogeno-C<sub>1</sub>-4-alkyl, or A represents halogen-substituted 3-pyridyl,

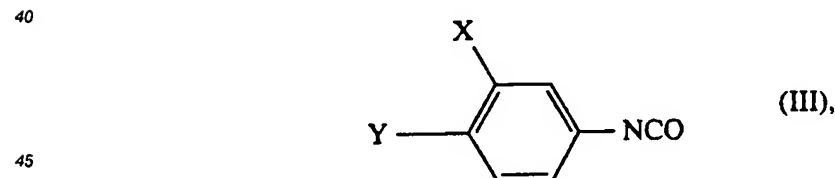
B represents phenyl which may be substituted by halogen, or B represents halogen-substituted 3-pyridyl, X represents hydrogen, halogen or halogeno-C<sub>1</sub>-4-alkyl, and Y represents hydrogen, halogen, C<sub>1</sub>-4-alkyl or halogeno-C<sub>1</sub>-4-alkyl, with the proviso that X and Y do not simultaneously represent hydrogen and that at least one of A and B represents halogen-substituted 3-pyridyl.

The pyrazolines of the formula (I) are obtained when

a) pyrazolines of the formula (II)



wherein A and B have the same meanings as mentioned above, are reacted with phenyl isocyanates of the formula (III)



wherein X and Y have the same meanings as mentioned above, in the presence of inert solvents.

The novel pyrazolines of the formula (I) exhibit powerful insecticidal properties.

Surprisingly, the pyrazolines according to the invention exhibit a substantially greater insecticidal action than those known from the prior art of the above-mentioned Japanese Laid-Open patent application. Particularly, the compounds according to the invention exhibit excellent insecticidal effects against Lepidoptera.

Referring to the formula (I) according to the invention, as well as the formula (II) and (III) of the intermediates used of the production thereof, halogen includes fluorine, chlorine, bromine and iodine, preferably fluorine, chlorine and bromine.



C<sub>1-4</sub>-alkyl and C<sub>1-4</sub>-alkyl moieties contained in C<sub>1-4</sub>alkoxy and in halogeno-C<sub>1-4</sub>-alkyl include methyl, ethyl, n-propyl, isopropyl, and n-(or iso-, sec- or tert-)butyl, preferably methyl, ethyl, n-propyl and isopropyl.

Among the pyrazolines according to the invention, of the formula (I), preferred compounds are those in which

- 5 A represents phenyl which may be substituted by at least one substituent selected from the class consisting of fluorine, chlorine, bromine, C<sub>1-4</sub>-alkyl, C<sub>1-4</sub>-alkoxy, difluoromethyl and trifluoromethyl, or A represents fluorine-, chlorine- or bromine-substituted 3-pyridyl,
- B represents phenyl which may be substituted by fluorine, chlorine, bromine, or B represents fluorine-, chlorine- or bromine-substituted 3-pyridyl,
- 10 X represents hydrogen, chlorine or trifluoromethyl, and Y represents hydrogen, halogen, C<sub>1-4</sub>-alkyl or fluoro-substituted methyl and with the proviso that X and Y do not simultaneously represent hydrogen atom, and that at least one of A and B represents halogen-substituted 3-pyridyl.

Very particularly preferred pyrazolines of the formula (I) are those in which

- A represents phenyl which may be substituted by at least one substituent selected from the class consisting of fluorine, chlorine, methyl, isopropyl, tert.-butyl, methoxy, trifluoromethyl or difluoromethyl, or
- 15 A represents chlorine- or bromine-substituted 3-pyridyl,
- B represents chlorine- or bromine-substituted 3-pyridyl,
- X represents hydrogen, chlorine or trifluoromethyl, and
- Y represents fluorine, chlorine, iodine, methyl, ethyl, isopropyl, tert.-butyl difluoromethyl or trifluoromethyl.

- 20 In addition to the compounds disclosed in the Preparation Examples the following compounds of general formula (I) are mentioned:

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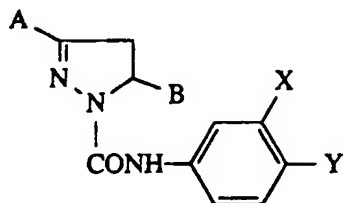
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Table 1



10	A	B	X	Y
	phenyl	6-Cl-3-pyridyl	H	Cl
	"	"	H	CF <sub>3</sub>
15	"	"	Cl	CF <sub>3</sub>
	4-F-phenyl	"	H	F
20	"	"	H	Cl
	"	"	H	I
	"	"	H	CH <sub>3</sub>
25	"	"	H	C <sub>2</sub> H <sub>5</sub>
	"	"	H	C <sub>3</sub> H <sub>7</sub> -iso
30	"	"	H	C <sub>4</sub> H <sub>9</sub> -tert
	"	"	H	CF <sub>3</sub>
35	"	"	H	CHF <sub>2</sub>
	"	"	Cl	CF <sub>3</sub>
40	"	"	CF <sub>3</sub>	H
	"	"	CF <sub>3</sub>	CF <sub>3</sub>
45	4-Cl-phenyl	"	H	F
	"	"	H	Cl
50	"	"	H	I
	"	"	H	CH <sub>3</sub>

55



Table 1 (continued)

	A	B	X	Y
5	4-Cl-phenyl	6-Cl-3-pyridyl	H	C <sub>2</sub> H <sub>5</sub>
	"	"	H	C <sub>3</sub> H <sub>7</sub> -iso
10	"	"	H	C <sub>4</sub> H <sub>9</sub> -tert
	"	"	H	CF <sub>3</sub>
	"	"	H	CHF <sub>2</sub>
15	"	"	Cl	CF <sub>3</sub>
	"	"	CF <sub>3</sub>	H
20	"	"	CF <sub>3</sub>	CF <sub>3</sub>
	3,4-Cl <sub>2</sub> -phenyl	"	H	Cl
25	"	"	H	CF <sub>3</sub>
	"	"	Cl	CF <sub>3</sub>
30	4-CH <sub>3</sub> -phenyl	"	H	CF <sub>3</sub>
	4-iso-C <sub>3</sub> H <sub>7</sub> -phenyl	"	H	CF <sub>3</sub>
	4-tert-C <sub>4</sub> H <sub>9</sub> -phenyl	"	H	CF <sub>3</sub>
35	4-CH <sub>3</sub> O-phenyl	"	H	CF <sub>3</sub>
	6-Cl-3-pyridyl	"	H	Cl
	"	"	H	CF <sub>3</sub>
40	"	"	Cl	CF <sub>3</sub>
	4-F-phenyl	5,6-Cl <sub>2</sub> -pyridyl	H	Cl
	"	"	H	CF <sub>3</sub>
45	4-Cl-phenyl	"	H	Cl

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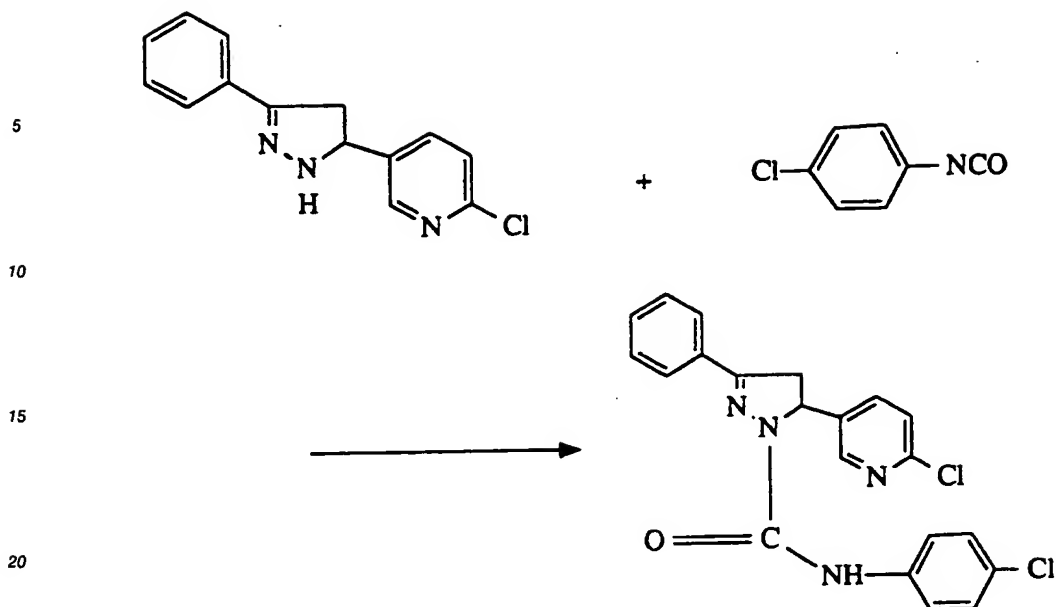
Table 1 (continued)

	A	B	X	Y
5	4-F-phenyl	5-Br-3-pyridyl	H	Cl
	"	"	H	CF <sub>3</sub>
10	4-Cl-phenyl	2-Cl-3-pyridyl	H	Cl
	"	"	H	CF <sub>3</sub>
15	6-Cl-3-pyridyl	phenyl	H	Cl
	"	"	H	CF <sub>3</sub>
	"	"	H	CHF <sub>2</sub>
20	"	"	Cl	CF <sub>3</sub>
	"	4-F-phenyl	H	Cl
25	"	"	H	CF <sub>3</sub>
	"	"	H	CHF <sub>2</sub>
30	"	"	Cl	CF <sub>3</sub>
	"	4-Cl-phenyl	H	Cl
	"	"	H	CF <sub>3</sub>
35	"	"	H	CHF <sub>2</sub>
	"	"	Cl	CF <sub>3</sub>
40	4-CF <sub>3</sub> -phenyl	6-Cl-3-pyridyl	H	CF <sub>3</sub>
	"	"	Cl	CF <sub>3</sub>
45	4-CHF <sub>2</sub> -phenyl	"	H	CF <sub>3</sub>
	"	"	Cl	CF <sub>3</sub>

50 If, for example, 3-phenyl-5-(6-chloro-3-pyridyl)-2-pyrazoline and 4-chlorophenyl isocyanate are used as starting materials, the course of the reaction can be represented by the following equation:

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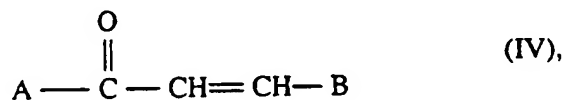




25 In process a), the starting material of the formula (II) means compounds based on the above definitions of A and B, preferably compounds based on the above preferred definitions.

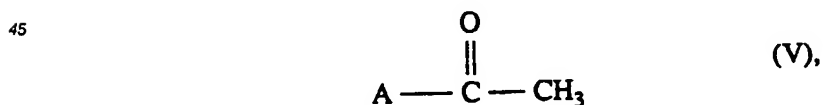
The starting materials of the formula (II) are novel compounds, and can be obtained in analogy to the process described in Japanese Laid-Open patent application No. 87028/1973, as illustrated in detail in the example below.

30 The starting materials of the formula (II) are obtained when the compounds of the formula (IV)

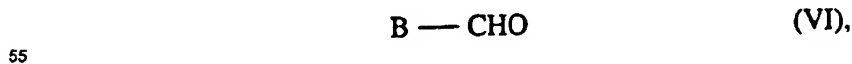


wherein A and B have the meanings stated above, are reacted with hydrazine hydrate, in the presence of inert solvents.

40 The compounds represented by the formula (IV) are novel compounds too, and can be obtained, for instance, when the compounds of the following formula (V)



50 wherein A has meaning stated above, are reacted with the compound of the following formula (VI)



wherein B has the meaning stated above, if appropriate in the presence of acid binding substances and in the presence of inert solvents.



The compounds represented by the formula (V) and (VI) are compounds known in the field of organic chemistry.

As representative examples of starting compounds of the formula (II) may be mentioned:

- 3-phenyl-5-(6-chloro-3-pyridyl)-2-pyrazoline,
- 5 3-(4-fluorophenyl)-5-(6-chloro-3-pyridyl)-2-pyrazoline
- 3-(4-chlorophenyl)-5-(6-chloro-3-pyridyl)-2-pyrazoline,
- 3-(6-chloro-3-pyridyl)-5-phenyl-2-pyrazoline,
- 3-(6-chloro-3-pyridyl)-5-(4-fluorophenyl)-2-pyrazoline, and
- 3-(6-chloro-3-pyridyl)-5-(4-chlorophenyl)-2-pyrazoline.

- 10 In process a), the starting compounds of the formula (III) mean compounds based on the above definitions of X and Y, preferably compounds based on the above preferred definitions.

The starting compounds are well known phenyl isocyanates. Representative examples of the formula (II) include:

- 4-chlorophenyl isocyanate,
- 15 4-trifluoromethylphenyl isocyanate,
- 4-difluoromethylphenyl isocyanate,
- 3-chlorophenyl isocyanate, and
- 3-chloro-4-trifluoromethylphenyl isocyanate.

In carrying out the process a) mentioned above, any inert solvent can be used as suitable diluent.

- 20 Examples of such diluents are water; aliphatic, cycloaliphatic and aromatic, optionally chlorinated, hydrocarbons such as pentane, hexane, cyclohexane, petroleum ether, ligroin, benzene, toluene, xylene, dichloromethane, chloroform, carbon tetrachloride, ethylene chloride, chlorobenzene, dichlorobenzene, and the like; ethers such as diethyl ether, methylethyl ether, di-isopropyl ether, di-butyl ether, propylene oxide, dimethoxyethane (DME), dioxane, tetrahydrofuran (THF) and the like; ketones such as acetone methylethyl
- 25 ketone (MEK), methyl-iso-propyl ketone, methyl-iso-butyl ketone (MIBK) and the like; nitriles such as acetonitrile, propionitrile, acrylonitrile, and the like; alcohols such as methanol, ethanol, iso-propanol, butanol, ethylene glycol and the like; esters such as ethyl acetate, amyl acetate, and the like; acid amides such as dimethyl formamide, diethyl acetamide, and the like; sulfones and sulfoxides such as dimethyl sulfoxide, sulfolane and the like; and, bases, for example, such as pyridine.

- 30 In the above mentioned process a), the reaction temperature can be varied within a substantially wide range. In general, the reaction is carried out at a temperature of from about 0° C to about 120° C, preferably from 10° C to about 40° C.

Further, the reaction is preferably carried out under normal pressure, although it is also possible to employ a higher or reduced pressure.

- 35 When the above mentioned process a) according to the present invention is carried out, use is made, for example, of the above mentioned compound (III) in the amount from 1.0 to 1.5 mols, preferably 1 to 1.2 mols, per one mol of the above mentioned compound (II), optionally in the presence of inert solvents such as acetonitrile, for example, to obtain the desired compounds of the formula (I).

- The active compounds of the formula (I) are well tolerated by plants, have a favorable level of toxicity to
- 40 warm-blooded animals, and can be used for combating arthropod pests, especially insects which are encountered in agriculture, in forestry, in the protection of stored products and of materials, and in the hygiene field. They are active against normally sensitive and resistant species and against all or some stages of development. The above-mentioned pests include:

- from the class of the Isopoda, for example, *Oniscus Asellus*, *Armadillidium vulgare* and *Porcellio scaber*;
- 45 from the class of the Diplopoda, for example, *Blaniulus guttulatus*;
- from the class of the Chilopoda, for example, *Geophilus carpophagus* and *Scutigera spec.*;
- from the class of the Symphyla, for example, *Scutigera immaculata*;
- from the order of the Thysanura, for example, *Lepisma saccharina*;
- from the order of the Collembola, for example, *Onychiurus armatus*;
- 50 from the order of the Orthoptera; for example, *Blatta orientalis*, *Periplaneta americana*, *Leucophaea maderae*, *Blattella germanica*, *Acheta domesticus*, *Grylotalpa* spp., *Locusta migratoria migratorioides*, *Melanoplus differentialis* and *Schistocerca gregaria*;
- from the order of the Dermaptera, for example, *Forficula auricularia*;
- from the order of the Isoptera, for example, *Reticulitermes* spp.;
- 55 from the order of the Anoplura, for example, *Phylloxera vastatrix*, *Pemphigus* spp., *Pediculus humanus corporis*, *Haematopinus* spp. and *Linognathus* spp.;
- from the order of the Mallophaga, for example, *Trichodectes* spp. and *Damalinea* spp.;
- from the order of the Thysanoptera, for example, *Hercinothrips femoralis* and *Thrips tabaci*;



from the order of the Heteroptera, for example, *Eurygaster* spp., *Dysdercus intermedius*, *Piesma quadrata*, *Cimex lectularius*, *Rhodnius prolixus* and *Triatoma* spp.;

from the order of the Homoptera, for example, *Aleurodes brassicae*, *Bemisia tabaci*, *Trialeurodes vaporariorum*, *Aphis gossypii*, *Brevicoryne brassicae*, *Cryptomyzus ribis*, *Aphis fabae*, *Doralis pomi*,  
 5 *Eriosoma lanigerum*, *Hyalopterus arundinis*, *Macrosiphum avenae*, *Myzus* spp., *Phorodon humuli*,  
*Rhopalosiphum padi*, *Empoasca* spp., *Euscelis bilobatus*, *Nephotettix cincticeps*, *Lecanium corni*, *Saissetia oleae*,  
*Laodelphax striatellus*, *Nilaparvata lugens*, *Aonidiella aurantii*, *Aspidiotus hederae*, *Pseudococcus* spp.  
 and *Psylla* spp.;

from the order of the Lepidoptera, for example, *Pectinophora gossypiella*, *Bupalus piniarius*, *Cheimatobia*  
 10 *brumata*, *Lithocolletis blancardella*, *Hyponomeuta padella*, *Plutella maculipennis*, *Malacosoma neustria*,  
*Euproctis chrysorrhoea*, *Lymantria* spp., *Bucculatrix thurberiella*, *Phyllocnistis citrella*, *Agrotis* spp., *Euxoa*  
 spp., *Feltia* spp., *Earias insulana*, *Heliothis* spp., *Spodoptera exigua*, *Mamestra brassicae*, *Panolis flammea*,  
*Prodenia litura*, *Spodoptera* spp., *Trichoplusia ni*, *Carpocapsa pomonella*, *Pieris* spp., *Chilo* spp., *Pyrausta*  
*nubialis*, *Ephestia kuehniella*, *Galleria mellonella*, *Cacoecia podana*, *Capua reticulana*, *Choristoneura*  
 15 *fumiferana*, *Clysia ambiguella*, *Homona magnanima* and *Tortrix viridana*;

from the order of the Coleoptera, for example, *Anobium punctatum*, *Rhizopertha dominica*, *Acanthoscelides*  
*obtectus*, *Acanthoscelides obtectus*, *Hylotrupes bajulus*, *Agelastica alni*, *Leptinotarsa decemlineata*, *Phaedon*  
*cochleariae*, *Diabrotica* spp., *Psylliodes chrysocephala*, *Epilachna varivestis*, *Atomaria* spp., *Oryzaephilus*  
*surinamensis*, *Anthonomus* spp., *Sitophilus* spp., *Otiorynchus sulcatus*, *Cosmopolites sordidus*, *Ceuthor-*  
 20 *thynchus assimilis*, *Hypera postica*, *Dermestes* spp., *Trogoderma* spp., *Anthrenus* spp., *Attagenus* spp.,  
*Lyctus* spp., *Meligethes aeneus*, *Ptinus* spp., *Niptus hololeucus*, *Gibbium psyllodes*, *Tribolium* spp.,  
*Tenebrio molitor*, *Agriotes* spp., *Conoderus* spp., *Melolontha melolontha*, *Amphimallon solstitialis* and  
*Costelytra zealandica*;

from the order of the Hymenoptera, for example, *Diprion* spp., *Hoplocampa* spp., *Lasius* spp., *Monomorium*  
 25 *pharaonis* and *Vespa* spp.;

from the order of the Diptera, for example, *Aedes* spp., *Anopheles* spp., *Culex* spp., *Drosophila melanog-*  
*aster*, *Musca* spp., *Fannia* spp., *Calliphora erythrocephala*, *Lucilia* spp., *Chrysomyia* spp., *Cuterebra* spp.,  
*Gastrophilus* spp., *Hypobosca* spp., *Stomoxys* spp., *Oestrus* spp., *Hypoderma* spp., *Tabanus* spp., *Tannia*  
 spp., *Bibio hortulanus*, *Oscinella frit*, *Phorbia* spp., *Pegomyia hyoscyami*, *Ceratitis capitata*, *Dacus oleae* and  
 30 *Tipula paludosa*.

The active compounds can be converted into the customary formulations, such as solutions, emulsions,  
 wettable powders, suspensions, powders, foams, pastes, granules, aerosols, natural and synthetic materials  
 impregnated with active compound, very fine capsules in polymeric substances, coating compositions for  
 use on seed, and formulations used with bunning equipment, such as fumigating cartridges, fumigating cans  
 35 and fumigating coils, as well as ULV cold mist and warm mist formulations.

These formulations may be produced in known manner, for example by mixing the active compounds  
 with extenders, that is to say liquid or liquefied gaseous or solid diluents or carriers, optionally with the use  
 of surface-active agents, that is to say emulsifying agents and/or dispersing agents and/or foam-forming  
 agents. In the case of the use of water as an extender, organic solvents can, for example, also be used as  
 40 auxiliary solvents.

As liquid solvents, diluents or carriers, there are suitable in the main, aromatic hydrocarbons, such as  
 xylene, toluene or alkyl naphthalenes, chlorinated aromatic or chlorinated aliphatic hydrocarbons, such as  
 chlorobenzenes, chloroethylenes or methylene chloride, aliphatic hydrocarbons, such as cyclohexane or  
 paraffins, for example mineral oil fractions, alcohols, such as butanol or glycol as well as their ethers and  
 45 esters, ketones, such as acetone, methyl ethyl ketone, methyl isobutyl ketone or cyclohexanone, or strongly  
 polar solvents, such as dimethylformamide and dimethyl-sulphoxide, as well as water.

By liquefied gaseous diluents or carriers are meant liquids which would be gaseous at normal  
 temperature and under normal pressure, for example aerosol propellants, such as halogenated hydrocar-  
 bons as well as butane, propane, nitrogen and carbon dioxide.

As solid carriers there may be used ground natural minerals, such as kaolins, clays talc, chalk, quartz,  
 attapulgite, montmorillonite or diatomaceous earth, and ground synthetic minerals, such as highly-dispersed  
 silicic acid, alumina and silicates. As solid carriers for granules there may be used crushed and fractionated  
 natural rocks such as calcite, marble, pumice, sepiolite and dolomite, as well as synthetic granules of  
 inorganic and organic meals, and granules of organic material such as sawdust, coconut shells, maize cobs  
 55 and tobacco stalks.

As emulsifying and/or foam-forming agents there may be used non-ionic and anionic emulsifiers, such  
 as polyoxyethylene-fatty acid esters, polyoxyethylene-fatty alcohol ethers, for example alkylaryl polyglycol  
 ethers, alkyl sulphonates, alkyl sulphates, aryl sulphonates as well as albumin hydrolysis products.



Dispersing agents include, for example, lignin sulphite waste liquors and methylcellulose.

Adhesives such as carboxymethylcellulose and natural and synthetic polymers in the form of powders, granules or latices, such as gum arabic, polyvinyl alcohol and polyvinyl acetate, can be used in the formulation.

It is possible to use colorants such as inorganic pigments, for example iron oxide, titanium oxide and Prussian Blue, and organic dyestuffs, such as alizarin dyestuffs, azo dyestuffs or metal phthalocyanine dyestuffs, and trace nutrients, such as salts of iron, manganese, boron, copper, cobalt, molybdenum and zinc.

The formulations in general contain from 0.1 to 95 percent by weight of active compound, preferably from 0.5 to 90 percent by weight.

The active compounds according to the invention can be present in their commercially available formulations and in the use forms, prepared from these formulations, as a mixture with other active compounds, such as insecticides, baits, sterilising agents, acaricides, nematocides, fungicides, growth-regulating substances or herbicides. The insecticides include, for example, phosphates, carbamates, carboxylates, chlorinated hydrocarbons, phenylureas, substances produced by microorganisms.

The active compounds according to the invention can furthermore be present in their commercially available formulations and in the use forms, prepared from these formulations, as a mixture with synergistic agents. Synergistic agent are compounds which increase the action of the active compounds, without it being necessary for the synergistic agent added to be active itself.

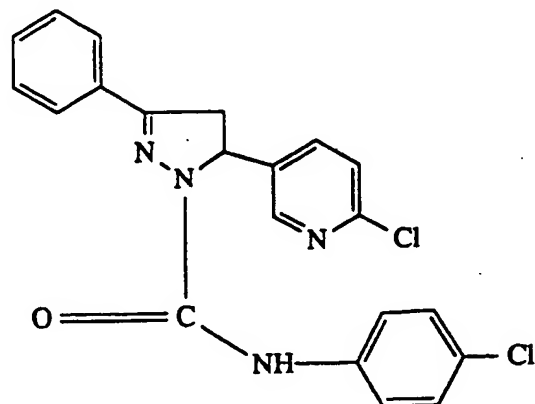
The active compound content of the use forms prepared from the commercially available formulations can vary within wide limits. The active compound concentration of the use forms can be from 0.0000001 to 100% by weight of active compound, preferably between 0.0001 and 1% by weight.

The compounds are employed in a customary manner appropriate for the use forms.

When used against hygiene pests and pests of stored products, the active compounds are distinguished by an excellent residual action on wood and clay as well as a good stability to alkali on limed substrates.

The preparation and use of the active compounds according to the invention can be seen from the following examples.

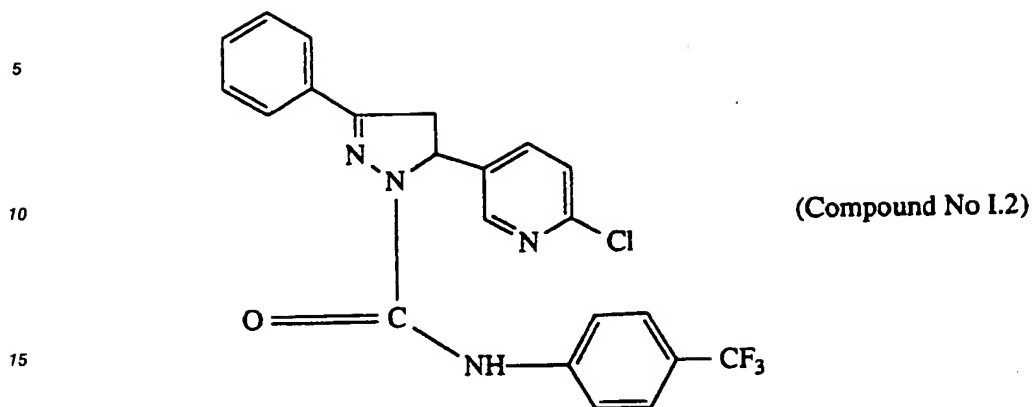
#### Example 1



(Compound No I.1)

3-Phenyl-5-(6-chloro-3-pyridyl)-2-pyrazoline (2.58 g) was dissolved in 10 ml of acetonitrile. The resulting solution was admixed with 4-chlorophenyl isocyanate (1.53 g) at room temperature, and stirred at room temperature for 10 hours, and then the solvent was distilled off under reduced pressure. The crude product thus formed was recrystallized from ethanol to give the 1-(4-chlorophenyl) carbamoyl-3-phenyl-5-(6-chloro-3-pyridyl)-2-pyrazoline (2.79 g). mp. 168-175°C.



Example 2

20 According to a procedure in analogy to that employed in Example 1, a reaction operation was carried out by using 4-trifluoromethylphenyl isocyanate, instead of 4-chlorophenyl isocyanate employed in Example 1, so that the 1-(4-trifluoromethylphenyl) carbamoyl-3-phenyl-5-(6-chloro-3-pyridyl)-2-pyrazoline (2.89 g) was produced.  
mp. 159-162°C.

25 According to the same way as those employed in the above-mentioned Examples, a number of compounds can be obtained as specifically shown in Table 2, wherein the compounds prepared in the aforementioned Examples are also shown.

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Table 2

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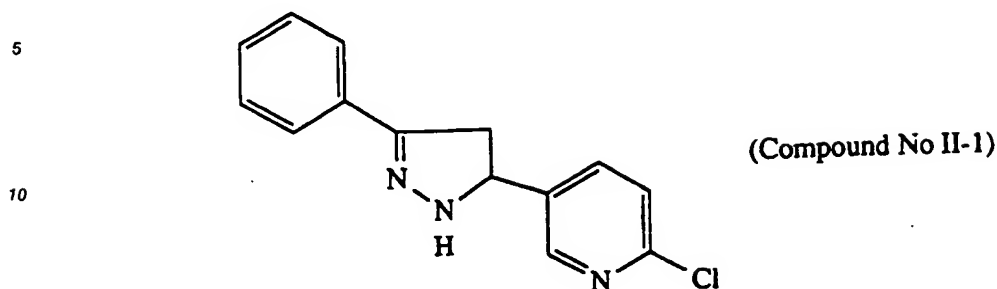
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(I)

Compound No.	A	B	X	Y	mp.°C
I.1	phenyl	6-Cl-3-pyridyl	H	Cl	168-175
I.2	"	"	H	CF <sub>3</sub>	159-162
I.3	4-F-phenyl	"	H	CF <sub>3</sub>	159-161
I.4	"	"	H	CHF <sub>2</sub>	181-184
I.5	"	"	Cl	CF <sub>3</sub>	178-181
I.6	4-Cl-phenyl	"	H	Cl	239-241
I.7	"	"	H	I	233-236
I.8	"	"	H	C <sub>3</sub> H <sub>7</sub> -iso	168-172
I.9	"	"	H	CF <sub>3</sub>	214-216
I.10	"	"	H	CHF <sub>2</sub>	227-230
I.11	"	"	Cl	CF <sub>3</sub>	172-177
I.12	"	"	CF <sub>3</sub>	H	226-227
I.13	3,4-Cl <sub>2</sub> -phenyl	"	H	Cl	164-177
I.14	"	"	H	CF <sub>3</sub>	142-162
I.15	4-CH <sub>3</sub> -phenyl	"	H	CF <sub>3</sub>	248-250
I.16	4-CH <sub>3</sub> O-phenyl	"	H	CF <sub>3</sub>	232-233
I.17	4-Cl-phenyl	"	H	F	204-206
I.18	"	"	H	CH <sub>3</sub>	225-229
I.19	6-Cl-3-pyridyl	6-Cl-3-pyridyl	H	CF <sub>3</sub>	187-188



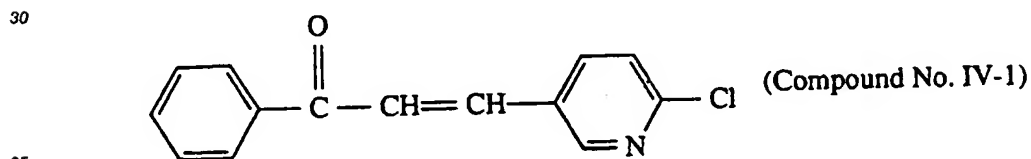
### Example 3 (synthesis of intermediate compound)



1-Phenyl-3-(6-chloro-3-pyridyl)-propenone (2.44 g) was dissolved in 20 ml of ethanol. The resultant solution was admixed with 0.5 ml of hydrazine hydrate, and heated under reflux for 3 hours. After the completion of the reaction, the solvent was distilled off under reduced pressure to give 3-phenyl-5-(6-chloro-3-pyridyl)-2-pyrazoline (2.58 g).

10	<sup>1</sup> H-NMR (90 MHz, δppm, CDCl <sub>3</sub> )	2.98 (1H, dd)
		3.53 (1H, dd)
		4.93 (1H, dd)
		6.00 (1H, m)
25		7.24-7.72 (7H, m)
		8.33 (1H, d)

#### Example 4 (synthesis of starting compound)

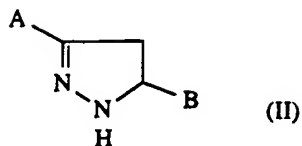


Acetophenone (12.0 g) and 6-chloro-nicotinic aldehyde (14.2 g) were dissolved in 100 ml of ethanol. To the resulting solution were dropwise added 20 ml of a 20% aqueous solution of sodium hydroxide at room temperature. The crystals thus formed were separated by filtration, washed with cold ethanol and dried in  
40 air to give 1-phenyl-3-(6-chloro-3-pyridyl)-propenone (19.9 g).  
mp. 186-189 ° C.

According to the same way as those employed in the above-mentioned Examples 3 and 4, a number of compounds can be obtained as specifically shown in Tables 3 and 4 respectively. These tables also show  
45 the compounds prepared in Examples 3 and 4.



Table 3



Compound No.	A	B	<sup>1</sup> H-NMR (90 MHz, CDCl <sub>3</sub> , ppm)
II-1	phenyl	6-Cl-3-pyridyl	2.98 (1H, dd) 3.53 (1H, dd) 4.93 (1H, dd) 6.00 (1H, m) 7.24-7.72 (7H, m) 8.33 (1H, d)
II-2	4-Cl-phenyl	6-Cl-3-pyridyl	2.93 (1H, dd) 3.50 (1H, dd) 4.96 (1H, dd) 5.20 (1H, m) 7.20-7.80 (6H, m) 8.33 (1H, d)
II-3	4-F-phenyl	6-Cl-3-pyridyl	2.90 (1H, dd) 3.50 (1H, dd) 4.95 (1H, dd) 6.00 (1H, m) 6.80-7.83 (6H, m) 8.33 (1H, d)
II-4	4-CH <sub>3</sub> -phenyl	6-Cl-3-pyridyl	2.33 (3H, s) 2.90 (1H, dd) 3.50 (1H, dd) 4.88 (1H, dd) 5.87 (1H, m) 7.07-7.60 (5H, m) 7.70 (1H, dd) 8.33 (1H, d)



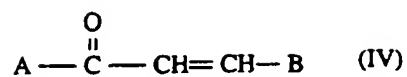
Table 3 (continued)

Compound No.	A	B H	<sup>1</sup> H-NMR (90 MHz, CDCl <sub>3</sub> , ppm)
II-5	4-tert-C <sub>4</sub> H <sub>9</sub> phenyl	6-Cl-3-pyridyl	1.33 (9H, s) 2.98 (1H, dd) 3.53 (1H, dd) 4.93 (1H, dd) 6.00 (1H, m) 7.20-7.75 (6H, m) 8.33 (1H, d)
II-6	6-Cl-3-pyridyl	6-Cl-3-pyridyl	2.95 (1H, dd) 3.57 (1H, dd) 5.03 (1H, dd) 6.47 (1H, m) 7.30 (1H, d) 7.33 (1H, d) 7.77 (1H, dd) 7.97 (1H, dd) 8.35 (1H, dd) 8.48 (1H, d)
II-7	6-Cl-3-pyridyl	4-Cl-phenyl	2.93 (1H, dd) 3.45 (1H, dd) 4.90 (1H, dd) 6.22 (1H, m) 7.20-7.35 (4H, m) 7.93 (1H, dd) 8.45 (1H, d)
II-8	3,4-Cl <sub>2</sub> -phenyl	6-Cl-3-pyridyl	oil



Table 4

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Compound No.	A	B	mp °C
IV-1	phenyl	6-Cl-3-pyridyl	186-189
IV-2	4-F-phenyl	6-Cl-3-pyridyl	152-154
IV-3	4-Cl-phenyl	6-Cl-3-pyridyl	173-175
IV-4	4-CH <sub>3</sub> -phenyl	6-Cl-3-pyridyl	180-182
IV-5	4-tert-C <sub>4</sub> H <sub>9</sub> -phenyl	6-Cl-3-pyridyl	165-166
IV-6	3,4-Cl <sub>2</sub> -phenyl	6-Cl-3-pyridyl	122-123
IV-7	4-Cl-3-pyridyl	6-Cl-3-pyridyl	227-228
IV-8	4-Cl-3-pyridyl	4-Cl-phenyl	168-169

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Biotest Example:Comparative compounds

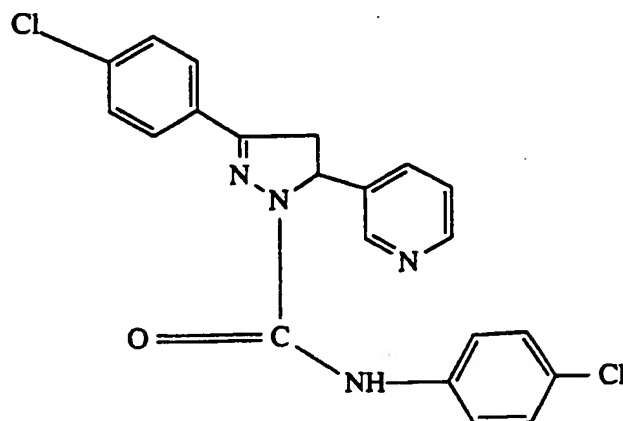
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C-1:

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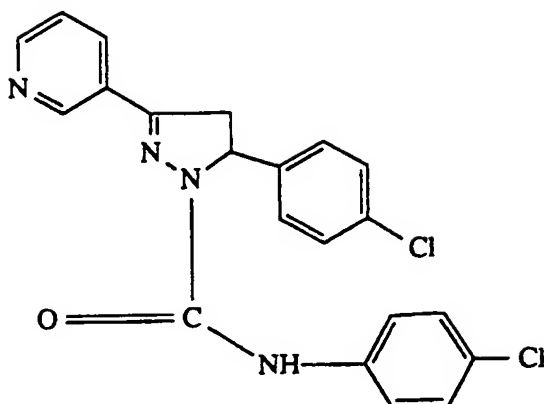


(disclosed in Japanese Laid-open Patent Application No. 87028/1973)

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C-2:





(also disclosed in Japanese Laid-open Patent Application No. 87028/1973)

#### Test Example 1

Biotest carried out against larvae of *Spodoptera litura*

Preparation of test formulation:

solvent: 3 parts by weight of xylene

Emulsifier: 1 part by weight of polyoxyethylene-alkylphenyl-ether

To prepare suitable formulations of active compounds, 1 part by weight of each of the active compounds was mixed with the above-mentioned amount of the emulsifier, and the mixture was diluted with water to the predetermined concentration.

Test Method:

Leaves of sweet potato plants (*Ipomoea batatas* Lam.) were soaked in a diluted aqueous solution of an active compound having a predetermined concentration, dried in air and placed on a dish with a diameter of 9 cm. 10 pieces of 3-instar larvae of *Spodoptera litura* were released into the dish, which was then placed in a green house having a constant temperature of 28°C. After 7 days, the number of the killed insects was determined to obtain the mortality of the insects.

The results are shown in Table 5.

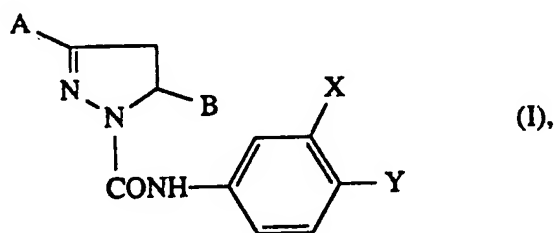


Table 5

Compound No.	Concentration of active compound (ppm)	Insect mortality after 7 days (%)
1.3	40	100
1.4	40	100
1.5	40	100
1.9	40	100
1.12	40	100
control		
C-1	1000	0
C-2	1000	0

## Claims

## 1. Pyrazolines of the formula (I)



wherein A represents phenyl which may be substituted by at least one substituent selected from the class consisting of halogen, C<sub>1-4</sub>-alkyl, C<sub>1-4</sub>-alkoxy and halogeno-C<sub>1-4</sub>-alkyl, or A represents halogen-substituted 3-pyridyl.

B represents phenyl which may be substituted by halogen, or B represents halogen-substituted 3-pyridyl,

X represents hydrogen, halogen or halogeno-C<sub>1-4</sub>-alkyl, and Y represents hydrogen, halogen, C<sub>1-4</sub>-alkyl or halogeno-C<sub>1-4</sub>-alkyl, with the proviso that X and Y do not simultaneously represent hydrogen and that at least one of A and B represents halogen-substituted 3-pyridyl.

2. The compounds of the claim 1 wherein A represents phenyl which may be substituted by at least one substituent selected from the class consisting of fluorine, chlorine, bromine, C<sub>1-4</sub>-alkyl, C<sub>1-4</sub>-alkoxy, difluoromethyl and trifluoromethyl, or A represents fluorine-, chlorine- or bromine-substituted 3-pyridyl, B represents phenyl which may be substituted by fluorine, chlorine, bromine, or B represents fluorine-,

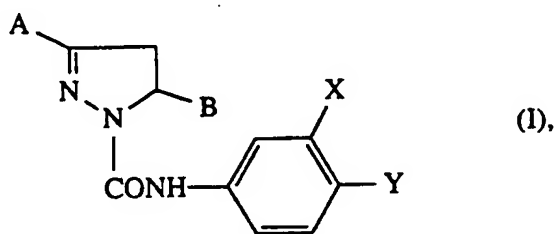


chlorine- or bromine-substituted 3-pyridyl,

X represents hydrogen, chlorine or trifluoromethyl, and Y represents hydrogen, halogen, C<sub>1-4</sub>-alkyl or fluoro-substituted methyl and with the proviso that X and Y do not simultaneously represent hydrogen, and that at least one of A and B represents halogen-substituted 3-pyridyl.

3. The compounds of the claim 1) or 2) wherein A represents phenyl which may be substituted by at least one substituent selected from the class consisting of fluorine, chlorine, methyl, isopropyl, tert-butyl, methoxy, trifluoromethyl or difluoromethyl or A represents chlorine- or bromine-substituted 3-pyridyl, B represents chlorine- or bromine-substituted 3-pyridyl, X represents hydrogen, chlorine or trifluoromethyl, and Y represents fluorine, chlorine, iodine, methyl, ethyl, isopropyl, tert-butyl, difluoromethyl or trifluoromethyl.

4. Process for the preparation of pyrazolines of the formula (I)



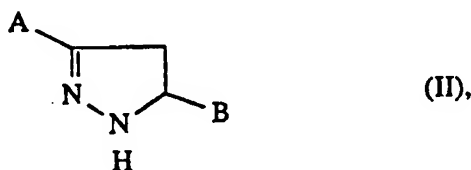
wherein A represents phenyl which may be substituted by at least one substituent selected from the class consisting of halogen, C<sub>1-4</sub>-alkyl, C<sub>1-4</sub>-alkoxy and halogeno-C<sub>1-4</sub>-alkyl, or A represents halogen-substituted 3-pyridyl.

B represents phenyl which may be substituted by halogen, or B represents halogen-substituted 3-pyridyl,

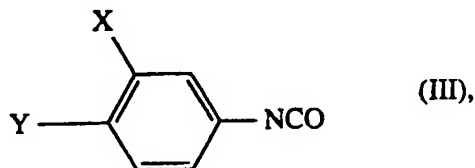
X represents hydrogen, halogen or halogeno-C<sub>1-4</sub>-alkyl, and Y represents hydrogen, halogen, C<sub>1-4</sub>-alkyl or halogeno-C<sub>1-4</sub>-alkyl, with the proviso that X and Y do not simultaneously represent hydrogen and that at least one of A and B represents halogen-substituted 3-pyridyl,

characterized in that

pyrazolines of the formula (II)



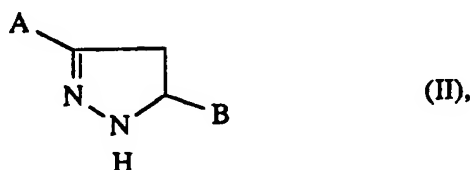
wherein A and B have the same meanings as mentioned above, are reacted with phenyl isocyanates of the formula (III)



wherein X and Y have the same meanings as mentioned above, in the presence of inert solvents.



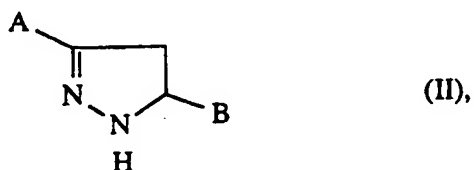
5. Insecticidal compositions, characterized in that they contain at least one pyrazoline of the formula (I) according to claim 1.
6. A method of combating insects, characterized in that pyrazolines of the formula (I) according to claim 1 are allowed to act on insects and/or their habitat.
7. Use of pyrazolines of the formula (I) according to claim 1 for combating insects.
8. Process for the preparation of insecticidal compositions, characterized in that pyrazolines of the formula (I) according to claim 1 are mixed with extenders and/or surface active agents.
9. Pyrazolines of the formula (II)



wherein A represents a phenyl group which may be substituted by at least one group selected from the class consisting of halogen, C<sub>1</sub>-4-alkyl, C<sub>1</sub>-4-alkoxy and halogeno-C<sub>1</sub>-4-alkyl, or A represents halogen-substituted 3-pyridyl.

B represents phenyl which may be substituted by halogen, or B represents halogen-substituted 3-pyridyl, with the proviso that at least one of A and B represents halogen-substituted 3-pyridyl.

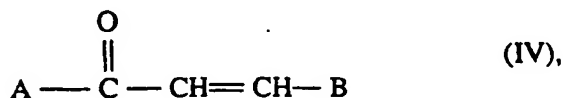
10. Process for the preparation of pyrazolines of the formula (II)



wherein A represents a phenyl group which may be substituted by at least one group selected from the class consisting of halogen, C<sub>1</sub>-4-alkyl, C<sub>1</sub>-4-alkoxy and halogeno-C<sub>1</sub>-4-alkyl, or A represents halogen-substituted 3-pyridyl,

B represents phenyl which may be substituted by halogen, or B represents halogen-substituted 3-pyridyl, with the proviso that at least one of A and B represents halogen-substituted 3-pyridyl, characterized in that

the compounds of the formula (IV)



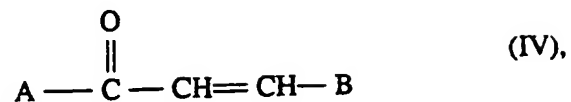
wherein A represents phenyl which may be substituted by at least one substituent selected from the class consisting of halogen, C<sub>1</sub>-4-alkyl, C<sub>1</sub>-4-alkoxy and halogen-C<sub>1</sub>-4-alkyl, or A represents halogen-substituted 3-pyridyl,

B represents phenyl which may be substituted by halogen, or B represents halogen-substituted 3-pyridyl, with the proviso that at least one of A and B represents halogen-substituted 3-pyridyl, are reacted with hydrazine hydrate,



in the presence of inert solvents.

11. The compounds of the formula (IV)



wherein A represents phenyl which may be substituted by at least one substituent selected from the class consisting of halogen, C<sub>1-4</sub>-alkyl, C<sub>1-4</sub>-alkoxy and halogeno-C<sub>1-4</sub>-alkyl, or A represents halogen-substituted 3-pyridyl,

B represents phenyl which may be substituted by halogen, or B represents halogen-substituted 3-pyridyl, with the proviso that at least one of A and B represents halogen-substituted 3-pyridyl,



(19)



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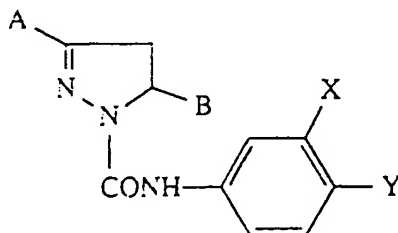
(11) Publication number:

**0 537 580 A3**

(12)

**EUROPEAN PATENT APPLICATION**(21) Application number: **92116943.9**(51) Int. Cl.<sup>5</sup>: **C07D 401/04, C07D 401/14,  
A01N 43/56**(22) Date of filing: **05.10.92**(30) Priority: **18.10.91 JP 297772/91**(43) Date of publication of application:  
**21.04.93 Bulletin 93/16**(84) Designated Contracting States:  
**BE CH DE ES FR GB IT LI NL**(86) Date of deferred publication of the search report:  
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**Konzernverwaltung RP**  
**Patentabteilung**  
**D-51368 Leverkusen Bayerwerk (DE)**(54) **Pyrazolines as insecticides.**

(57) Novel pyrazolines of the formula (I)



wherein A represents a phenyl group which may be substituted by at least one substituent selected from the class consisting of halogen, C<sub>1-4</sub>alkyl, C<sub>1-4</sub>alkoxy and halogeno-C<sub>1-4</sub>alkyl, or A represents halogen-substituted 3-pyridyl,

B represents phenyl which may be substituted by halogen, or B represents halogen substituted 3-pyridyl,

X represents hydrogen, halogen or halogeno C<sub>1-4</sub>alkyl, and

Y represents hydrogen, halogen, C<sub>1-4</sub>alkyl or halogeno-C<sub>1-4</sub>alkyl, with the proviso that X and Y do not simultaneously represent hydrogen atom, and that at least one of A and B represents halogen-substituted 3-pyridyl.

**EP 0 537 580 A3**



**EP 0 537 580 A3**

The new compounds exhibit powerful insecticidal properties.





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## EUROPEAN SEARCH REPORT

Application Number

EP 92 11 6943

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X,D	DE-A-2 304 584 (N.V. PHILIPS) 16 August 1973 * compounds 90,91 * * claim 1 *	1-8	C07D401/04 C07D401/14 A01N43/56
A	US-A-4 140 787 (BASF AKTIENGESELLSCHAFT) 20 February 1979 * examples 1,2 *	1-8	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			C07D
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 24 AUGUST 1993	Examiner DE JONG B.S.
<b>CATEGORY OF CITED DOCUMENTS</b>			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons * : member of the same patent family, corresponding document	